COLOR REMOVAL FROM SYNTHETIC DYE AND TEXTILE WASTEWATERS USING ADSORBENT PREPARED FROM PSYLLIUM HUSK.

By

SOMAIA M. O. TAYEH

This dissertation is submitted to

UNIVERSITI SAINS MALAYSIA

As partial fulfillment of requirements for the degree of

School of Civil Engineering

Universiti Sains Malaysia

Engineering Campus

June 2012

ACKNOWLEDGEMENTS

First of all, I would like to express my grateful to Allah SWT for all his gifts, that this thesis was completely finished. Then my grateful also dedicated to my parents for all their pray and supporting me to go forward in my study.

I would like to express my grateful thanks to my supervisor Dr. Irvan Dahlan for his guidance, motivation and endless supports during this project.

I cannot forget to thank my small family, my husband Bassam and my children Wala`, Bara` and Shahd, for their continued patience and encouragement throughout all my study.

Finally, I present a lot of thanks for all people who contributed with their helps directly or indirectly in finishing my thesis.

Thank you all very much.

Somaia

TABLE OF CONTENTS

APPENDICES

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

Penyingkiran Warna dari Pencelup Sintetik dan Air Sisa Tekstil Menggunakan Bahan Penjerap Disediakan dari Sekam Psyllium

ABSTRAK

Penyingkiran warna dari efluen tekstil telah diberikan banyak perhatian dalam beberapa tahun lepas oleh proses penjerapan menggunakan adsorbents kos rendah. Dalam kajian ini, bahan penjerap sekam psilium/$CoFe_2O_4$ (PH/CFO), disintesiskan melalui satu langkah mudah laluan refluks dan telah digunakan sebagai bahan penjerap untuk penyingkiran warna dari pelarut pencelup sintetik dan air buangan tekstil. Kajian kelompok menunjukkan bahawa kecekapan penyingkiran terbaik bahan penjerap berada di pH 9.0, suhu 30^{o}C (untuk pelarut sintetik) dan 40^{o}C (untuk air buangan tekstil), kadar goncangan sebanyak 150 rpm (untuk pelarut sintetik) dan 280rpm (untuk air buangan tekstil), dan masa sentuh 2 jam. Bahan penjerap PH/CFO menunjukkan kecekapan penyingkiran lebih tinggi pada kecekapan awal pencelup yang tinggi. Pada masa yang sama, kecekapan bahan penjerap bertambah dengan berkurangnya jumlah bahan penjerap yang digunakan. Data eksperimen berpadanan baik dengan model Langmuir dengan keupayaan jerapan satu lapisan 188.7mg/g. Penjerapan ilmu kinetik didapati mengikuti model kinetik pseudo- aturan kedua. Analisis saiz partikel dan pemerhatian SEM disediakan dan dibelanjakan penjerap telah dijalankan, analisis saiz zarah menunjukkan taburan saiz zarah yang homogenus untuk kedua-dua sampel. Pemerhatian SEM menunjukkan bahawa zarah pewarna yang didepositkan seragam ke permukaan PH/CFO penjerap.

Colour Removal from Synthetic Dye and Textile Wastewater Using Adsorbent Prepared from Psyllium Husk

ABSTRACT

Color removal from textile effluents has been given much attention in the last few years by the adsorption process using low cost adsorbents. In this study, psyllium husk/$CoFe_2O_4$ adsorbent, (PH/CFO), was synthesized by a simple one-step refluxing route and was used as adsorbent for the removal of color from synthetic dye solution and textile wastewater. The batch experiments showed that the best removal efficiency of the adsorbent was at pH 9.0, temperature 30^{o}C (for synthetic wastewater) and at 40^{o}C (for textile wastewater), shaking rate 150 rpm (for synthetic wastewater) and 280rpm (for textile wastewater), and at contact time 2 hours. The PH/CFO adsorbent showed higher removal efficiency at higher initial dye concentrations. At the same time, the adsorbent efficiency was increasing by decreasing the amount of adsorbent used. The experimental data fitted well with the Langmuir model with a monolayer adsorption capacity of 188.7mg/g. The adsorption kinetics was found to follow pseudo-second-order kinetic model. The particle size analysis and SEM observations of prepared and spent adsorbent where carried out, particle size analysis showed a homogenous particle size distribution for both samples. SEM observations showed that the dye particles deposited uniformly onto the surface of PH/CFO adsorbent.

CHAPTER ONE

INTRODUCTION

1.1 Background

Due to the increase in the world population and development of industrial applications, environmental pollution problem became very important, especially wastewater pollution problem. Communities produce both liquid and solid wastes. The liquid waste -wastewater- is essentially the water supply of the community after it has been used in a variety of applications. Wastewater handling, disposal & treatment are serious worldwide problem. Many industrial and agricultural activities use water in an excessive way. However, it is now well known that the fresh water resources are limited and fragile, so they must be protected.

Discharge of sanitary wastewater, industrial effluent and agricultural field's runoff can be the main source of freshwater pollution. This causes many diseases for human, and it is known that 70-80% of illness in developing countries is related to water contamination, particularly for children and women (WHO/UNICEF, 2000).

Textile industries consume large volumes of water and chemicals for wet processing of textiles. The chemical reagents used are very diverse in chemical composition, ranging from inorganic compound to polymers and organic compound (Correia et al., 1994). The color is an evident indicator of water pollution by the dyes. Industrial dye effluents are visible even at concentrations lower than 1 mg/l. Moreover, some dyes and their degradation products are carcinogenic (Ahn et al., 1999). Also, some dyes are harmful to aquatic life in rivers where they are discharged. Since, dye can reduce light penetration into the water thereby decreasing the efficiency of photosynthesis in aquatic plants and hence having adverse impact on their growth (Che Ani, 2004)

1.2 Problem statement

Textile wastewater is generally high in both color and organic content. Effluents discharged from dyeing industries are highly colored and they can be toxic to aquatic life in receiving waters (Lee et al., 1999, Kadirvelu et al., 2003). Color removal from textile effluents has been given much attention in the last few years, not only because of its potential toxicity, but mainly due to its visibility problems (Morais et al., 1999). The total dye consumption of the textile industry worldwide is in excess of 10^7 kg/year, and an estimated 90% of this ends up on fabrics. Consequently, 1000 tonnes/year or more of dyes are discharged into waste streams by the textile industry worldwide (Ahmad et al., 2007).

Development of the appropriate techniques for treatment of dye wastewater is important for the protection of natural water. To eliminate dyes from aqueous colored effluents and reduce their ecological consequences, several biological and chemical techniques have been proposed: anaerobic/aerobic degradation (Ahmed et al., 2007), coagulation/flocculation (Papić et al., 2000) and also oxidative/reductive chemical and photochemical processes (Lucas and Peres, 2006). Due to relatively high operating costs and low removal efficiencies using the above-mentioned processes, textile, pulp and paper industries seldom apply these to treat their effluents.

Among several chemical and physical methods, the adsorption has been found to be superior to other techniques in water reuse methodology because of its capability for adsorbing a broad range of different types of adsorbates efficiently, and simplicity of design. Many researchers researched for cheaper substitutes, which are relatively inexpensive, and are at the same time endowed with reasonable adsorptive capacity. These studies include the use of coal, fly ash, activated clay, palm-fruit bunch, Bagasse pith, cellulose-based waste, peat, bentonite, slag and fly ash, rice husk, activated sludge, etc (Ahmad et al., 2007).

Psyllium husk has not been investigated as adsorbent for color removal from dye solutions and textile wastewater. This research studied the adsorption for color removal from synthetic and real textile wastewater, using an adsorbent prepared from psyllium husk.

1.3 Objectives of the study

The main aim of this study is to apply the adsorption technique as a treatment method to remove dyes and color from synthetic dye and real textile wastewaters, by using an adsorbent prepared from an inexpensive and readily available material which is psyllium husk. Also, the study aims to achieve the following measureable objectives:

1- To prepare and characterize adsorbent from psyllium husk using quaternized and magnetic methods.

2- To investigate the ability of the best psyllium husk adsorbent for removal of color from synthetic dye and textile wastewater under various operating conditions (initial dye concentration, amount of sorbent, shaking rate, contact time, pH, temperature).

3- To determine the kinetic behavior and isotherms for the adsorption process of color onto psyllium husk adsorbent.

1.4 Scope of study

The scope of this study is the removal of color from textile waste water and from synthetic solution contained direct blue 71 dye. The best adsorbent was selected from many types of adsorbents prepared from psyllium husk. Characterization of psyllium husk adsorbent was carried out with Particle Size Distribution analyzer (Mastersizer 2000) and Scanning Electron Microscopy (SEM).

Batch experiments were carried out for the adsorption of dye onto the psyllium husk adsorbent. The effect of the following parameters was investigated: adsorbent amount, initial dye concentration, contact time, shaking rate, pH, and temperature. Moreover the best fitting adsorption isotherm models were examined using the most widely applied isotherm models. Adsorption isotherms are helpful in demonstrating the extent of homogeneity of the adsorption sites and the affinity of these sites towards the adsorbed molecules.

1.5 Organization of the thesis

There are five chapters in the thesis **Chapter one** provides an introduction and background of the study. **Chapter two** presents a review of the literature. It reviews the textile wastewater: its characteristics and treatment, Dyes: their types and impacts, Adsorption: process, kinetics and isotherm models, Types of adsorbents: activated carbon and psyllium husk. **Chapter three** covers the experimental part. This chapter is divided into 4 sections. The 1^{st} section presents the materials, chemicals, equipments and adsorbent preparation methods used in the experiments. The 2^{nd} section explains the preliminary study to select the best adsorbent. The 3^{rd} section explains the main batch studies (applied on synthetic and real textile wastewater). And the 4^{th} section is for the characterization of the adsorbents. **Chapter four** presents the experimental results together with the discussion. It is grouped into 4 sections. The 1^{st} section presents the results for preliminary study. The 2^{nd} section gives results of the main batch studies for synthetic dye solution and real textile wastewater. The 3^{rd} section presents the results of kinetic and equilibrium studies. And the 4^{th} section gives the results for the characterization of the adsorbents. Finally, **Chapter five** gives the conclusions and recommendations of the thesis.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

Wastewater pollution creates many problems of turbidity, odor, color, and many other problems. The quality of waste water can be characterized by physical, chemical and biological parameters (Metcalf and Eddy, 2003). Physical parameters include color, odor, temperature, solids, turbidity, density and conductivity. Chemical parameters include biochemical oxygen demand (BOD), chemical oxygen demand (COD), pH, acidity, alkalinity, chlorides, sulphates, nitrogen (organic, ammonia, nitrite, and nitrate), metals such as mercury (Hg), lead (Pb), chromium (Cr), nickel (Ni), copper (Cu), and zinc (Zn). Biological parameters include the presence of bacteria and other microorganisms. Fifth Schedule of Environmental Quality Act 1974, under Environmental Quality (Industrial Effluent) Regulation 2009, listed the maximum acceptable conditions for discharge of industrial effluent or mixed effluent of standard A and B as shown in Table 2.1.

2.2 Textile wastewater

The textile industry, apart from being an important contributor to the economy of many countries, is also a major source of various liquid, solid and gaseous wastes. This kind of industrial activity can have a negative impact on the environment, both in terms of pollutant discharge as well as of water and energy consumption. Although the amount of water used and wastewater generated is largely dependent upon the specific type of operations followed, in general, dyeing, washing, and finishing operations spend the greatest demand (Gurnham, 1965). For instance, and as reported by that the volume of wastewater generated by dyeing and finishing operations ranged from 73 to 167m^3 per ton of product (Fongsatitkul et al., 2004).

Table 2.1: Acceptable concentrations for discharge of industrial effluent or mixed effluent of standards A and B (DOE, 2012).

Parameter	**Unit**	**Standard**	
		A	**B**
Temperature	^{o}C	40	40
pH Value	–	6.0-9.0	5.5-9.0
BOD_5 at 20^{o}C	mg/L	20	50
COD (Textile industry)	mg/L	80	250
Suspended Solids	mg/L	50	100
Mercury	mg/L	0.005	0.05
Cadmium	mg/L	0.01	0.02
Chromium,Hexavalent	mg/L	0.05	0.05
Chromium, Trivalent	mg/L	0.20	1.0
Arsenic	mg/L	0.05	0.10
Cyanide	mg/L	0.05	0.10
Lead	mg/L	0.10	0.5
Copper	mg/L	0.20	1.0
Manganese	mg/L	0.20	1.0
Nickel	mg/L	0.20	1.0
Tin	mg/L	0.20	1.0
Zinc	mg/L	2.0	2.0
Boron	mg/L	1.0	4.0
Iron (Fe)	mg/L	1.0	5.0
Silver	mg/L	0.1	1.0
Aluminium	mg/L	10	15
Selenium	mg/L	0.02	0.5
Barium	mg/L	1.0	2.0
Fluoride	mg/L	2.0	5.0
Formaldehyde	mg/L	1.0	2.0
Phenol	mg/L	0.001	1.0
Free Chlorine	mg/L	1.0	2.0
Sulphide	mg/L	0.50	0.50
Oil and Grease	mg/L	1.0	10
Ammoniacal Nitrogen	mg/L	10	20
Colour	ADMI*	100	200

*ADMI–American Dye Manufacturers Institute

2.2.1 *Textile wastewater characteristics*

Textile wastewater is characterized mainly by measurements of biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids (SS) and dissolved solids (DS). Typical characteristics of textile industry wastewater are presented in Table 2.2, which show a large extent of variation from plant-to-plant and sample-to sample. As presented in Table 2.2, COD values of textile wastewater are extremely high as compared to other parameter. In most cases BOD/COD ratio of the textile wastewater is around 0.25 that implies that the wastewater contains large amount of non-biodegradable organic matter (Al-Kdasi et al., 2004).

Table 2.2: Textile Industry Wastewater Characteristics (Al-Kdasi et al., 2004)

Parameters	Values
pH	7.0 - 9.0
Biological Oxygen Demand (mg/L)	80 - 6000
Chemical Oxygen Demand (mg/L)	150 -12000
Total Suspended Solids (mg/L)	15 - 8000
Total dissolved solids (mg/L)	2900 - 3100
Chloride (mg/L)	1000 - 1600
Total Kjeldahl Nitrogen (mg/L)	70 - 80
Color (Pt-Co)	50 - 2500

2.2.2 *Dyes*

Dyes are synthetic organic compounds that are increasingly being produced and used as colorants in many industries worldwide, including textile, plastic, paper, etc (Crini, 2006, Wu and Tseng, 2008). The wastewater generated by the processes of these industries usually contains up to around 10% of used dye (Forgacs et al., 2004). The total dye consumption of the textile industry worldwide is more than 10^7 kg/year, 90% ends on fabrics. So, 1000 tones/year of dyes are discharged into waste streams. (Ahmad et al., 2007).

2.2.3 Types of dyes

There are many structural varieties of dyes, such as, acidic, basic, disperse, azo, diazo, anthroquinone based and metal complex dyes. The azo dyes, characterized by having an azo group consisting of two nitrogen atoms (─N≡N─), are the largest class of dyes used in textile industry (Sun et al., 2007). Inside the azo dyes there are wide types of dyes, namely acid, reactive, disperse, vat, metal complex, mordant, direct, basic and sulphur dyes. Also, there are many structural varieties of dyes that fall into either the cationic, nonionic or anionic type. Anionic dyes are the direct, acid and reactive dyes (Mishra and Tripathy, 1993). Nonionic dyes refer to disperse dyes because they do not ionize in an aqueous medium (Baughman and Perenich, 1988).

2.2.4 Impact of dyes

Dyes are the most problematic pollutants of textile wastewaters. This fact occurs because after the basic dyeing process is finished, 10% - 15% of the textile dyes is lost in wastewater stream during dyeing operation (Muruganandham and Swaminathan, 2004).

Most of the dyes are toxic and carcinogenic compounds; they are also recalcitrant and thus stable in the receiving environment, posing a serious threat to human and environmental health (Crini, 2008). Accordingly, to protect humans and the receiving ecosystem from contamination, the dyes must be eliminated from the dye-contained wastewaters before being released into the environment.

2.2.5 Direct blue71 (DB71)

Direct dyes are commonly used in the printing process of the textile industry. Most of the printing process-textile factories belong to the small factory group (home-made textile products) (Gupta et al., 1992, Hu, 1996, Wong and Yuen, 1996, Slokar and Majcen Le Marechal, 1998, Soares et al., 2001). One of the direct dyes is direct blue71, with the molecular formula $C_{40}H_{27}N_7Na_4O_{13}S_4$ (molecular weight 1029.88), Figure 2.1 shows the structure of direct blue71.

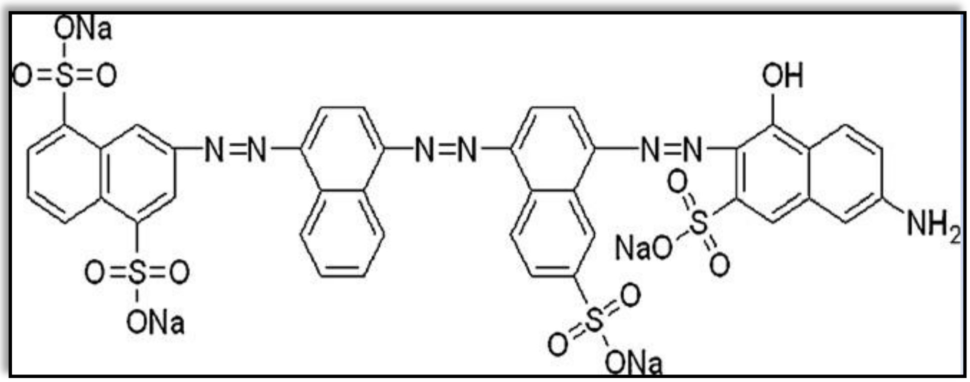

Figure 2.1: Structure of direct blue71 (DB71) (Habibi and Mikhak, 2012).

The most widely used methods of dye removal from dye-containing industrial effluents, have been classified under three categories: chemical, physical and biological. Currently the main methods of textile dye treatment are physical and chemical means concentrating on cheaper and effective alternatives.

2.2.6 Color Scales (APHA and ADMI)

2.2.6a APHA/PtCo standard:

The American Public Health Association (APHA) Index was developed in the 1890s as a visual indicator of the purity of wastewater, where color is due to the presence of naturally-occurring organic materials such as leaves, bark, roots, humus, and peat. Today, APHA is used as a metric for purity in the chemical, oil, plastics, and pharmaceutical industries. This scale serves to quantify the appearance of yellowness, a visual indicator of product degradation due to light and/or heat, the presence of impurities, and the effects of processing. APHA – recommended standard of 1 color unit being equal 1mg/L platinum as chloroplatinate ion, The test of measuring color for this scale is Platinum-Cobalt Standard Method, and it shows the results in mg/L Pt-Co. (Lab)

2.2.6b ADMI Scale:

The American Dye Manufacturer's Institute (ADMI) scale was developed for the measurement of wastewater containing dyestuffs and textile effluents. This scale may be used on clear liquids of any color. The ADMI adopted the Platinum-Cobalt Standard of the American Public Health Association (APHA) as the standard for color value. Although this standard is yellow, the ADMI method works for all hues.

ADMI units are based on the total color difference of APHA solutions from distilled water. Distilled water has a value of zero in ADMI units, as it does in APHA units. An ADMI value of 500 is assigned to a solution having a total color difference from distilled water equal to the total color difference from distilled water of the APHA stock solution, which has an APHA value of 500 (Lab).

2.2.7 Textile wastewater treatment

The treatment of textile wastewater is very complex, because the raw materials processed and the intermediate products manufactured vary greatly in their nature and composition. The composition of waste varies even in same industry as a result of transition from one raw material to another and continual changing of process lines and also due to type of fabric manufactured. Before treatment, a separation of different types of wastewater into following group takes place (Yadav and Dhir, 2008):

i. Concentrated liquids (e.g., dyeing, finishing, printing)

ii. Medium polluted wastes (e.g., washing, rinsing)

iii. Low to zero polluted wastes (e.g., cooling water).

The various methods of treatment of textile wastewater have been used as physical treatment, physico-chemical treatment, biological treatment and advanced oxidation processes.

2.2.6a Physical Treatment

Physical processes such as sedimentation, equalization, segregation, filtration (e.g., sand filter) are capable of removing the suspended solids, however the removal of organic load is found to be negligible. Physical processes followed by physico-chemical or biological process show good results (Fiola and Luce, 1998).

2.2.6b Physico-chemical Treatment

There are many physico-chemical processes have been used for textile wastewater treatment such as chemical coagulation/ flocculation ($Fe^{2+/3+}$, Al^{3+}, polyelectrolyte) (Papić